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ULTRASONIC PROPERTIES OF AMORPHOUS POLYSTYRENES

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An ultrasonic experiment is described that incorporates measurement of the dynamic storage and loss moduli together with that of specific volume as a means to characterize the sample, at temperatures from - 150 to 300°C, and pressures up to 2 kbars. Results are presented that were obtained on two amorphous polystyrenes of different molecular weights. The discussion centers on the description of the modulus and points out to the importance of configurational entropy.

INTRODUCTION

Studies on polymer viscoelasticity are usually carried out with the various approaches of low frequency rheology. These techniques have become authoritative, however, they are by no means unique, nor universal. In this perspective, ultrasonics has proven a powerful tool for studies on elastic solids and viscous liquids and gases, and therefore appears as an interesting approach to viscoelasticity. However the technique has seldom been used for polymer studies, even though all available reports indicate that the ultrasonic properties of polymers could be described in terms of viscoelasticity. A survey of the literature will be published elsewhere, at this time the following reviews and books are relevant: Hartmann (1), Pethrick (2), Herzfeld (3), Litovitz (4), Christensen (5), Beyer (6). Rheological measurements are made at different frequencies under isothermal conditions, whereas ultrasonic experiments are performed at a constant frequency over a range of temperatures. Because polymer properties are both time and temperature dependent, a means is required to define the thermodynamic state of the material, before one can attempt to correlate the low and high frequency results. The fact that this problem has been addressed only rarely, Morita (7), Paddison (8), has lead to uncertainties and ambiguities.

In this paper, we briefly describe our apparatus, which provides access to the storage and loss moduli, and also incorporates

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a simultaneous measurement of specific volume as a means to characterize the thermodynamic state of the material, in the temperature range from - 150 to 300°C, and at pressures of up to 2 kbars. We present results on amorphous polystyrenes having different molecular weights. The discussion focusses on the description of the intermolecular interaction, and examines the validity of Rao's law in its application to polymers.

EXPERIMENTAL APPROACH AND TECHNIQUE

The ultrasonic approach to materials' characterization, essentially involves propagating low amplitude stress waves, and studying the characteristics of propagation, (velocity, v, attenuation, a, and frequency, $f = \omega/2\pi$) in relation to the properties of the sample. These techniques usually refer to frequencies in the MH_z range, where piezoelectric transducers are most efficient, and serve both for the production and detection of stress.

Fig. (1) illustrates the basic principle used in the experiment. The accurate measurement of the time delay Δt, between successive echoes, allows one to compute the velocity of sound, while the attenuation is obtained from their relative amplitudes:

$$v = \Delta t/2e \qquad (1)$$

$$a = - (1/2e) \ln (E_1/E_0) \qquad (2)$$

where e is the sample thickness. In practice v is given in cm/s, and a in cm^{-1}, or in dB/cm, where 1.0 cm^{-1} = 8.686 dB/cm.

Different types of transducers generate either shear or compressional (longitudinal) deformations. Shear waves are described by the complex shear modulus ($G^* = G' + iG''$), while longitudinal waves are associated with the longitudinal modulus ($L^* = L' + iL''$). The longitudinal modulus for uniaxial compression results from a combination of hydrostatic compression and pure shearing, $L^* = B^* + 4G^*/3$ where B^* is the complex bulk modulus. The equations that govern the propagation of sound in viscoelastic media are given by (Ref. 3,4,5):

$$G' = v_s^2/V \quad \text{and} \quad G'' = 2a_s v_s^3/\omega V \qquad (3)$$

$$L' = v_l^2/V \quad \text{and} \quad L'' = 2a_l v_l^3/\omega V \qquad (4)$$

where v_l, v_s and a_l, a_s are the velocity and attenuation of longitudinal and shear waves respectively, V is the specific volume, and ω the angular frequency ($\omega = 2\pi f$).

The assembly in Fig. (1) was installed in a jig that allowed for the axial displacement of the buffer rods to compensate sample expansion. Also, allowance was made for the application of an axial clamping pressure that was controlled to $\mp$ 1.0 bar in the range up to 2 kbars. The axial displacement was monitored to $\mp$ 1.0 μm, thus giving access to the thickness, volume, and speci-

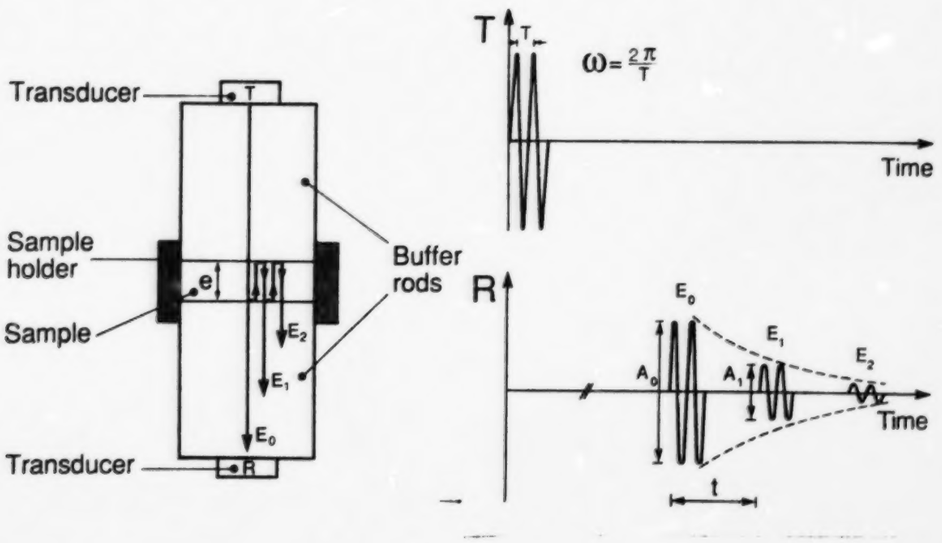

Figure 1: Schematic of basic ultrasonic experiment.

fic volume. Finally, a heating/cooling system was attached to the buffer rods as a means to scan the temperature from -150 to 300°C. The control system allowed one to program heating/cooling rates from 50°C/min to 1°C/hr, and constant temperature conditions of ∓ 0.1°C. The setup was under full computer control, and the collection of all data concerning length, temperature, pressure and acoustic signal was accomplished every 10 s.

RESULTS: AMORPHOUS POLYSTYRENE

Samples and Experimental Procedure Two atactic polystyrenes with different molecular weights and molecular weight distributions were investigated. The first (PS1) was a Dow Chemical Styron 685D, with number average molecular weight Mn = 130,000 g/mol and Mw/Mn = 2. The second material (PS2) was manufactured by Pressure Chemicals with Mn = 9,000 g/mol and Mw/Mn = 1. This sets PS1 and PS2 respectively above, and below the critical limit for chain entanglements, which for polystyrene set in above M_c ≈ 38 000 g/mol, Ferry (9). The sample of thickness e ≈ 3 mm was annealed in the apparatus for 30 min at 190°C. A fixed thermal history was used throughout so that the results could be reproduced: a pressure p = 225 bars was applied to the liquid and the sample was cooled to 20°C at a rate of 25°C/min; measurements were carried out with the same pressure on heating at a constant rate dT/dt = 2°C/min. The data in Fig. (2) were obtained with longitudinal waves at a frequency f = 1.75 MHz.

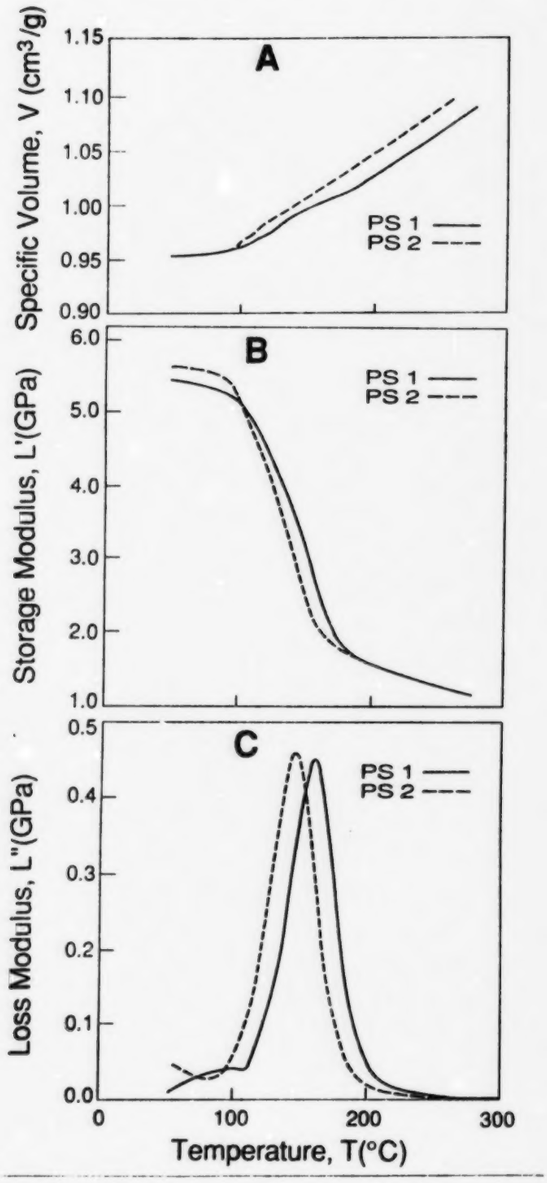

Figure 2: Specific Volume, Storage and Loss Moduli (f = 1.75 MHz) for polystyrene PS1 with Mn = 130,000 and PS2 = 9000.

Specific volume, Fig. (2A) At the lower temperatures, the specific volume, V, and thermal expansion $\alpha = \partial \ln V / \partial T$ are quite similar for both glasses, with $\alpha_g \approx 1.3 \times 10^{-4}/°C$. When increasing temperature, the specific volume suddenly rises much faster. Here, for operational purposes, we define a critical temperature T_V at the intercept of the linear extrapolations of the data above and below the breaks in the V-T curves: $T_V(PS1) = 105°C$, and $T_V(PS2) = 96°C$. As seen in Fig. (2A), V(PS1) slowly departs from linear behaviour in the vicinity of $T_V(PS2)$, however the rise becomes "definite" only upon nearing $T_V(PS1) = 105°C$. In the region up to $T_V(PS1) + 35°C$ measurements can be reproduced provided the same thermal history is maintained: the material is clearly out of equilibrium. Above 140°C, the behaviour is no longer influenced by thermal history. In this region, the molecular structure adapts rapidly to changes in temperature. The material appears to be in equilibrium, with an expansivity typical of a polymer liquid: $\alpha_l = 5.6 \times 10^{-4}/°C$. At still higher temperature, $T \approx 175°C$, yet another change occurs in the V-T curve. This event is often referred to as the liquid-liquid transition, T_{ll}, Boyer (10). Above T_{ll}, the thermal expansion remains constant, $\alpha_{ll} = 8.6 \times 10^{-4}/°C$. For PS2, the increase in specific volume begins at T_V (PS2) = 96°C, and is more sudden, and already at T_V (PS2) + 17°C the thermal expansivity equals that of PS1 above T_{ll}.

The behaviour near T_V (PS1) and T_V (PS2) is typical of the "glass transition phenomenon". The glass transition is usually described (Ref. 9) as a kinetic process of volume contraction, and therefore dilatometry is a basic experiment for the determination of the glass transition temperature Tg. Since the glass transition is a rate process, the value for Tg is not unique, and one should refer to a region of temperatures for the transition. However, for operational purposes, Tg is usually defined as the temperature for the marked rise of specific volume, in which case $T_V = Tg$. On the other hand Tg is known to be dependent upon molecular weight: $Tg(°C) = 100 - 10^5/M$ (Ref. 9). The present data yields $Tg(PS1) - Tg(PS2) = 9.0°C$, in good agreement with the expected value $\Delta Tg = 9.0°C$, Boyer (11).

Ultrasonic storage and loss moduli, Fig. (2B, 2C) Below Tg, the storage modulus for PS1 and PS2 decreases linearly with increasing temperature: $\partial \ln L'_g / \partial T \approx -12.0 \times 10^{-4}/°C$. This behaviour is common to solids and is interpreted in terms of anharmonicity. For the polymer glass however $\partial \ln L'_g / \partial T$ is about 20 times greater, indicative of the highly anharmonic character of the glass. On this subject, it may be pointed out that upon further cooling, or on relaxing the pressure, the PS2 sample was not stable. In this region of temperature the loss modulus, L"(PS1) in Fig. (2C), shows a small increase remeniscent of the β feature observed in rheology techniques. On the other hand the behaviour for L"(PS2) must be considered with respect to the structural instability of the PS2 glass.

As temperature exceeds what appears to be a critical value, T_L, the storage modulus L' suddenly collapses, while the loss modulus L" begins to increase. Examination shows that T_L (PS1) = 105°C and T_L (PS2) = 97°C, and are virtually identical to

Tg(PS1) and Tg(PS2). The decrease of the storage modulus at Tg, reflects the collapse of the structure, while the increase of the loss modulus indicates that the structural rearrangements are accompanied by irreversible losses.

It is known that close to Tg, the dominant characteristic times τ are long (hours, minutes, seconds). Consequently Tg depends on the time scale, or frequency for the measurement. In the present experiment the time scale for probing the long relaxation times is given by the rate of heating $dT/dt = 2.0°C/min$. In regards to the high frequency sound wave, the slow molecular movements appear as if frozen in. Therefore the ultrasound measures the instantaneous, unrelaxed or frozen in properties of the material as they evolve with time and temperature.

This behaviour is expected to prevail up to where the material reaches thermal equilibrium with respect to temperature, near Tg(PS1) + 35°C ≈ 140°C, and Tg(PS2) + 17°C ≈ 123°C. Indeed, the storage moduli in Fig. (2B) both show a linear decrease up to 140°C for PS1, and 123°C for PS2, where a different regime is established. Thereafter L'(PS1) and L'(PS2) describe inverted S curves that merge near 186°C, where $\partial \ln L'_{11}/\partial T = -36.0 \times 10^{-4}/°C$. Correspondingly the loss moduli L", in Fig. (2C), both describe strong maximum before decreasing to vanishingly small values.

Such a behaviour is typical of a relaxation process. In the region above 140°C for PS1 and 123°C for PS2, the materials are in equilibrium with respect to temperature, and the time scale for the experiment is given by the frequency of the sound wave $\omega = 2\pi f$. Then the complex modulus, $L^* = L^*(\omega) = L'(\omega) + iL''(\omega)$ may be analyzed in terms of the usual model for the linear viscoelastic solid:

$$L'(\omega) = L_R + (L_U - L_R) \int H(\tau) \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} \, d\tau \qquad (5)$$

$$L''(\omega) = (L_U - L_R) \int H(\tau) \frac{(\omega\tau)}{1 + (\omega\tau)^2} \, d\tau \qquad (6)$$

where $H(\tau)$ represents the distribution of relaxation times, L_U is the unrelaxed modulus corresponding to $\omega\tau \gg 1$ (lower temperatures), and L_R is the relaxed modulus for the limit where $\omega\tau \ll 1$ (higher temperatures). In the lower temperature region, $L' \simeq L_U$ and the material appears as an elastic solid, while at the higher temperatures, $L' \simeq L_R$ and the material behaves as a viscous liquid. In this sense only, one may speak of the relaxation peak as being a transition phenomenon. At much lower frequencies, the maximum in the loss modulus occurs close to Tg, and it is often the practice to identify the temperature for the maximum with Tg. However it must be kept in mind that the two phenomena are quite distinct. The glass transition Tg involves a change in the thermodynamic state of the material, whereas the relaxation process does not. Here, this is clearly evidenced since the maximum for

L" occurs in a region of temperature where the material is in thermodynamic equilibrium.

DISCUSSION

Our results are in good overall agreement with previous reports from the literature, Thurn (12), Wada (13), Kono (14), also references (1) and (7). One of the outstanding features of the present experiment is that it allows for full control of the pressure/volume/temperature/time (p, V, T, t) parameters, thus providing means to study dynamic behaviour in terms of well defined thermodynamic properties. In this context our results show that the different regimes for the propagation of sound emulate those for specific volume, and thus confirm the importance of specific volume in determining polymer behaviour.

Usually the abnormally large expansivity and compressibility of liquids are attributed to the formation of "free volume", V_f, due to structural irregularities, in addition to Vo, the "volume occupied" by the molecules: $V = Vo + V_f$. Although the concept is vague and poorly defined, experience has shown that the specific volume of liquids is governed by the free volume fraction, $f = V_f/V$. Relative to its value at To and po, f is written in terms of α_f and β_f, the expansivity and compressibility associated with V_f:

$$f = fo + \alpha_f (T - To) - \beta_f (p - po) \qquad (7)$$

In attempt to relate the ultrasonic modulus, L', to the specific volume, we may assume L' to be a function of both temperature and volume, $L' = L'(V,T)$. Specializing to the region outside of the relaxation, where the polymer is a liquid, we may write $L' = B' + 4G'/3 \approx B$ (bulk modulus), and therefore:

$$dB = (\partial B/\partial V)_T \, dV + (\partial B/\partial T)_V dT \qquad (8)$$

$$(dB/dT)_p = \alpha V(\partial B/\partial V)_T + (\partial B/\partial T)_V \qquad (9)$$

In most cases it may be assumed, Broadhurst (15), that the entropic contribution $\partial B/\partial T$ is small and can be safely neglected. Also, one usually considers that B is mainly determined by the interaction potential, which for a van der Waals material is written:

$$U(V) = - D_1(V/Vo)^{-m/3} + D_2(V/Vo)^{-n/3} \qquad (10)$$

In the case where $V \approx V_o$, and after some tedious algebra, one arrives at:

$$(\partial \ln B/\partial T)p \approx - \alpha(n + m + 3)/3 \qquad (11)$$

Now it has been found (Ref. 15) that for polymers $m \approx 6$ and $n \approx 12$, such that:

$$(\partial \ln B/\partial T)p = - 7\alpha \qquad (12)$$

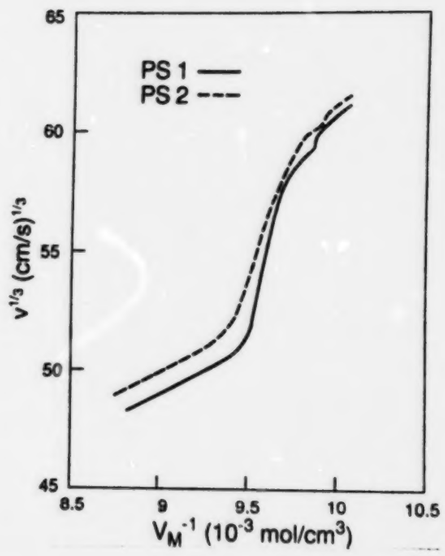

Figure 3: Rao's law, Eq. 13 for PS1 and PS2.

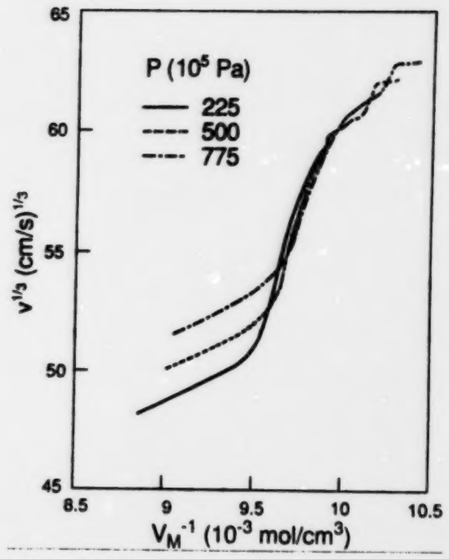

Figure 4: Rao's law, Eq. 13 for PS1 at p = 225, 500 and 775 bars.

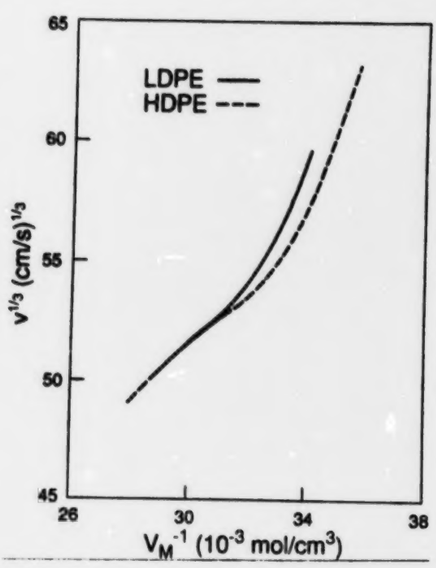

Figure 5: Rao's law for polyethylenes, high density (HDPE) and low density (LDPE).

$$v_1^{1/3} V_M = R \qquad (13)$$

where Eq. 13, Rao's (16) law, results from integrating Eq. 12, using $B = v_1^2/V$ for the velocity and $V_M = VM$ for the molar volume. Rao's law has been used extensively (Ref. 6) for liquids where it was found that R is a characteristic constant for a given molecular species. Furthermore, it was suggested that Eq. 13 also applies to polymers, Van Krevelen (17).

We analyzed our data according to Rao's rule, Eq. 13, in Fig. (3). Although PS1 and PS2 may be described with the same R, the curves do not coincide. On the other hand, the results in Fig. (2A) suggest that Eq. 13 should be modified to account for the different free volume fractions, f(PS2), f(PS1). In support of this, Fig. (4) shows results for PS2 at different pressures (p = 225, 500 and 775 bars) and evidently a better description would include free volume. Finally, Fig. (5) illustrates results for a linear high density polyethylene (HDPE) and a branched low density polyethylene (LDPE). For these materials the specific volumes and expansivities of the melt are equal, and it may be assumed that the free volumes are also equal. In this case, v and V apparently obey Rao's rule. However, it must be noted that although this may be valid over the limited range for the melt, there is no justification for using Rao's correlation at lower temperatures where the material is a solid.

On the other hand, comparing our results in Fig. (2) to Eq. 12, we find $(\partial \ln L'/\partial T)/\alpha \approx -4.2$ for PS and -4.0 for PE, which is quite different from the value, -7, in Eq. 12. Obviously, one is not justified in neglecting the entropic term in Eq. 9. In fact, using the present data allows us to evaluate:

$$(\partial L'/\partial T)_V/(\partial L'/\partial T)_p = 1 + \alpha L'(\partial L'/\partial p)_T/(\partial L'/\partial T)_p \approx -2.0$$

This shows that the modulus is not a function of volume only (intermolecular spacing) and that entropy plays an important role. Finally, our results strongly suggest that the formation of the glass corresponds to a freezing in of configurational structure in the liquid.

CONCLUSION

We have described an apparatus that allows measuring the ultrasonic complex moduli of polymers over a wide range of temperatures and pressures. The instrument incorporates a simultaneous measurement of specific volume for the characterization of the thermodynamic state of the sample. Results obtained on two polystyrenes having different molecular weights were presented. The behaviour for the storage and loss moduli, $L^* = L' + iL''$, was shown to be intimately related to specific volume, reflecting the irreversible structural changes in the material on going through the glass transition. The discussion pointed out to the importance of free volume and configurational entropy for the description of the bulk modulus. Also, it was shown that Rao's law for usual liquids is not directly applicable to polymers.

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